

Electronic Supplementary Information (ESI)

Electroactive Sulfur-Rich Materials Obtained *via* Inverse Vulcanization of a Diallylsilyl- Functionalized Ferrocene

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1. Experimental section

Materials. All reactions and compound manipulations were performed in an oxygen- and moisture-free Ar atmosphere using standard Schlenk techniques. *n*-hexane was distilled under argon from P₂O₅ and purged immediately before use. Ferrocene, *n*-butyllithium (*n*-BuLi, 1.6 M solution in *n*-hexane), tetramethylethylenediamine (TMEDA), allyl(chloro)dimethylsilane and elemental sulfur (Merk-Sigma Aldrich) were used as received. Silica gel (60 mesh, 40-63 Å, Merck-Sigma Aldrich) was used for column chromatography purifications. ZnCl₂, Cd(ClO₄)₂, and Hg(ClO₄)₂ were obtained from Merk-Sigma Aldrich.

Equipment. Attenuated Total Reflection Infrared (ATR-FTIR) spectra were recorded on a Jasco FT/IR-410 spectrometer. Samples of rubber-like materials were pressed before analysis. Elemental analyses were performed by a Dumas combustion at 1000 °C, in a LECO CHNS-932 elemental analyzer equipped with a MX5 Mettler Toledo microbalance. Solution NMR spectra were recorded on a Bruker Avance III-HD NANOBAV 300 MHz spectrometer. Chemical shifts were reported in parts per million (δ) with reference to CDCl₃ residual solvent resonances for ¹H (δ 7.26 ppm) and ¹³C (δ 77.2 ppm). Solid-state ¹³C and ²⁹Si CP/MAS NMR experiments were carried out on a Bruker AV-400-WB spectrometer operating at 100.6 MHz. Chemical shifts were reported in parts per million (δ). In the ¹³C CP/MAS NMR spectra, adamantane (CH₂ 29.5 ppm) was used as a secondary reference, relative to TMS as a primary reference. In the ²⁹Si CP/MAS NMR spectra, kaolin (-91.4 ppm) was used as a secondary reference, relative to tetrakis(trimethylsilyl)silane as the primary reference. Qualitative and quantitative Total X-Ray Fluorescence analyses (TXRF)¹ were performed with a benchtop S2 PicoFox TXRF spectrometer from Bruker Nano GmbH (Germany). TXRF system was equipped with a molybdenum X-ray source working at 50 kV and 600 μ A, a multilayer monochromator with 80% reflectivity at 17.5 keV (Mo K α), an XFlash SDD detector with an effective area of 30 mm², and an energy resolution better than 150 eV for Mn K α . Commercial Spectra v.7.5.3 software package from Bruker was used for deconvolution and integration. For the TXRF measurements, samples were digested at high pressure and temperature using microwave acid digestion technology. An acid mixture of HNO₃ (3 mL) and HCl (0.5 mL) was used for around 5 mg

¹ R. Fernández-Ruiz, TXRF Spectrometry in the Bioanalytical Sciences: A Brief Review. *X-Ray Spectrom.*, 2022, **51**, 279–293 (DOI: 10.1002/xrs.3243).

of sample, both placed in quartz reaction vessels. The UltraWAVE digestion system, working to 240 °C for a plateau of 15 min, was applied as Fernández-Ruiz et al.² MALDI-TOF mass spectra were recorded using a Bruker-Ultraflex III TOF/TOF mass spectrometer equipped with a Neodymium Yag laser emitting at 355 nm. Dichloromethane solutions of the matrix (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile, DCTB, 10 mg/mL) and CH₂Cl₂ solutions of the corresponding compound (1 mg/mL) were mixed in a 20:5 ratio. Then, the mixture (0.5-1 μL) was deposited on the target plate using the dried droplet method. The positive ion and the reflector mode were used for these analyses. The thermogravimetric analyses were performed using a TGA Q-500 instrument coupled with an EGA oven. Samples (5–10 mg) were loaded in platinum pans. The measurements were carried out under N₂ (90 mL min⁻¹) with a heating rate of 10 °C min⁻¹. X-ray photoelectron spectroscopy (XPS) was performed under ultra-high vacuum conditions (10⁻¹⁰ mbar) on a SPECS GmbH System equipped with a PHOIBOS 150 9MCD energy analyzer. A double anode X-ray source (Al/Mg), operating at a pressure of 200 W and a voltage of 12 kV, was used. Samples were first degassed in a pre-vacuum chamber, at room temperature for several hours, before being transferred to the analysis chamber. The survey scans were recorded at a pass energy of 50 eV and the higher resolution scans at a pass energy of 20 eV. SPECS sample holders made of 1.4571 stainless steel were used. The samples were fixed to the sample holders using double-sided conductive copper tape (ANAME). Data analysis was performed using the software Winspec and fitted with Shirley's background. Scanning electron microscopy (SEM) images were acquired in a Hitachi S3000N microscope with a coupled EDX from Oxford Instruments, INCAx-sight model. The samples were frozen and grounded using liquid N₂ to break the rubber-like material into small fragments to observe either the surface or the fracture edges of the material. Then, they were metallized in a Sputter Quórum Q150T-S with gold coating.

Electrochemical measurements. Cyclic voltammetry (CV) and square wave voltammetry (SWV) experiments were recorded on an Autolab PGSTAT302F potentiostat. CH₃CN (SDS, spectrograde) was freshly distilled from calcium hydride under Ar. Tetra-*n*-butylammonium hexafluorophosphate, [*n*-Bu₄N][PF₆], and ammonium

² R. Fernández-Ruiz, M. J. Redrejo, E. J. Friedrich K., N. Rodríguez and R. Amils, Suspension Assisted Analysis of Sulfur in Petroleum Coke by Total-Reflection X-Ray Fluorescence. *Spectrochim. Acta B: At. Spectrosc.*, 2020, **174**,105997.

hexafluorophosphate, $[\text{NH}_4][\text{PF}_6]$, (both Alfa-Aesar), which were purified by recrystallization from ethanol and dried in vacuum at 60 °C, were used as the supporting electrolytes in acetonitrile and water, respectively. The supporting electrolyte concentration was 10^{-1} M. Solutions of the redox-active species, which are soluble in acetonitrile, were 10^{-3} M and were purged with nitrogen and kept under an inert atmosphere throughout the measurements. A conventional three-electrode cell connected to an atmosphere of pre-purified nitrogen was used. The counter electrode was a coiled Pt wire, and the reference electrode was a BAS saturated calomel electrode (SCE). The working electrodes employed were a gold-disk electrode ($A = 0.02 \text{ cm}^2$, Bioanalytical Systems) for the soluble samples, or a carbon paste electrode in the case of the insoluble polymers obtained by inverse vulcanization. The Au-working electrode was polished on a Buehler polishing cloth with Metadi II diamond paste for about 3 min followed by sonication in absolute ethanol, rinsed thoroughly with purified water and acetone, and allowed to dry. The carbon paste working electrode consists of a hollow electrode ($A = 0.20 \text{ cm}^2$, Metrohm) filled with a hybrid paste. The hybrid was prepared by hand-mixing, with a mortar and pestle, 40.0 mg of high purity carbon paste oil base (>99.9%, Bioanalytical Systems) with 13.0 mg of the corresponding electroactive material and 1 drop of mineral oil (Nujol, density = 0.88 g cm^{-3}). The resulting paste was then inserted into the hollow electrode. Under our conditions, the ferrocene redox couple $[\text{FeCp}_2]^{0/+}$ is +0.437 V with the Au-working electrode, and +0.540 V with the carbon paste working electrode, vs. SCE in $\text{CH}_3\text{CN}/0.1 \text{ M } [n\text{-Bu}_4\text{N}][\text{PF}_6]$. No IR compensation was used. SWV was performed using frequencies of 10 Hz.

For the electrochemical sensing process of cations, a Milli-Q H_2O solution of $[\text{NH}_4][\text{PF}_6]$ (4 mL, 10^{-1} M) was placed in an electrochemical cell, purged with nitrogen for at least 10 min, and stirred. Stirring was stopped, and a nitrogen atmosphere was maintained above the solution while the experiment was in progress. Metal ion recognition studies were performed by consecutive additions of variable amounts of each cation salt in the water solutions. These experiments were carried out employing the carbon paste working electrode prepared with material **2**. The modified electrode was cleaned by sonication in water after each recognition process.

Synthesis of 1,1'-bis(dimethylallylsilyl)ferrocene (1). In a three-necked, round-bottom flask equipped with a gas inlet, a pressure equalizing addition funnel, an Allihn condenser topped with gas inlet and bubbler, and a teflon-covered magnetic stir bar, a solution of ferrocene (17.8 mmol, 3.308 g) and TMEDA (36.7 mmol, 5.5 mL) in 60 mL of

n-hexane was treated dropwise with *n*-BuLi (38.4 mmol, 24.0 mL of 1.6 M solution in *n*-hexane). The mixture was stirred for 18 h and an orange precipitate was formed, the dilithium salt $\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{Li})_2\cdot\text{TMEDA}$, which was filtrated and washed with *n*-hexane. Additional *n*-hexane (50 mL) was added to the resulting pale orange precipitate and the suspension was cooled to $-35\text{ }^\circ\text{C}$. A 20 mL *n*-hexane solution of allyl(chloro)dimethylsilane (35.7 mmol, 5.4 mL) was added dropwise under continuous stirring. After 30 min, the reaction was allowed to warm to room temperature and was stirred for 12 additional hours. The reaction mixture was filtered, and the volatiles of the filtrate were removed under vacuum. The dark orange oily product obtained was purified by column chromatography on silica gel (3 cm x 27 cm), using *n*-hexane as eluent. A first yellow band containing unreacted ferrocene was eluted, and subsequently, a second major orange band was obtained. Solvent removal afforded the desired compound **1** as an analytically pure, air-stable, orange liquid.

Yield: 3.90 g (57%). ^1H NMR: (CDCl_3 , 300 MHz, ppm): δ 5.79 (m, 2H, $\text{CH}=\text{CH}_2$), 4.88 (m, 2H, $\text{CH}=\text{CH}_{\text{trans}}\text{H}_{\text{cis}}$), 4.84 (m, 2H, $\text{CH}=\text{H}_{\text{trans}}\text{H}_{\text{cis}}$), 4.34 and 4.12 (pseudo-t, 4H+4H, C_5H_4), 1.68 (d, 4H, $\text{CH}_2\text{-CH}=\text{CH}_2$), 0.23 (s, 12H, CH_3); ^{13}C NMR: (CDCl_3 , 75 MHz, ppm): δ 135.0 ($\text{CH}=\text{CH}_2$), 113.2 ($\text{CH}=\text{CH}_2$), 73.1, 71.3 and 70.5 (C_5H_4), 24.9 ($\text{CH}_2\text{-CH}=\text{CH}_2$), -2.4 (CH_3); ^{29}Si NMR: (CDCl_3 , 59 MHz, ppm): δ -3.5 ppm; ATR-IR: 1630 cm^{-1} (ν ($\text{C}=\text{C}$)), 1420 cm^{-1} (ν ($\text{C}=\text{C}$)_{asym Fc}), 1248 cm^{-1} (δ (C-Si)), 1163 cm^{-1} (ν ($\text{C}=\text{C}$)_{sym Fc}), 1036 cm^{-1} (δ (C-H)_{Fc}), 992 y 931 cm^{-1} (δ ($=\text{CH}$)), 817 cm^{-1} (ν (C-Si), δ (C-H)_{Fc}); MS (MALDI-TOF): m/z 382.2 [M^+].

General inverse vulcanization reaction procedure: obtention of materials 2 and 3. In a 10 mL round-bottom flask, under a flow of argon, elemental sulfur and monomer **1** (100 mg), in 50:50 and 70:30 weight ratios, were vigorously stirred and properly heated at the corresponding temperature (greater than the sulfur melting point, $120\text{ }^\circ\text{C}$), using an oil bath. The reaction time was counted once the sulfur was completely melted and until the formation of a red rubber-like semisolid was noticed. After cooling, each ferrocenyl-containing polysulfide material (**2** for the 50:50 and **3** for the 70:30 wt %) was thoroughly washed with CH_2Cl_2 , to remove any unreacted compound **1**, and with CS_2 to remove S_8 , until colorless solutions were obtained in both cases. Materials **2** and **3** were appropriately dried.

2. Spectra and analysis of compound 1

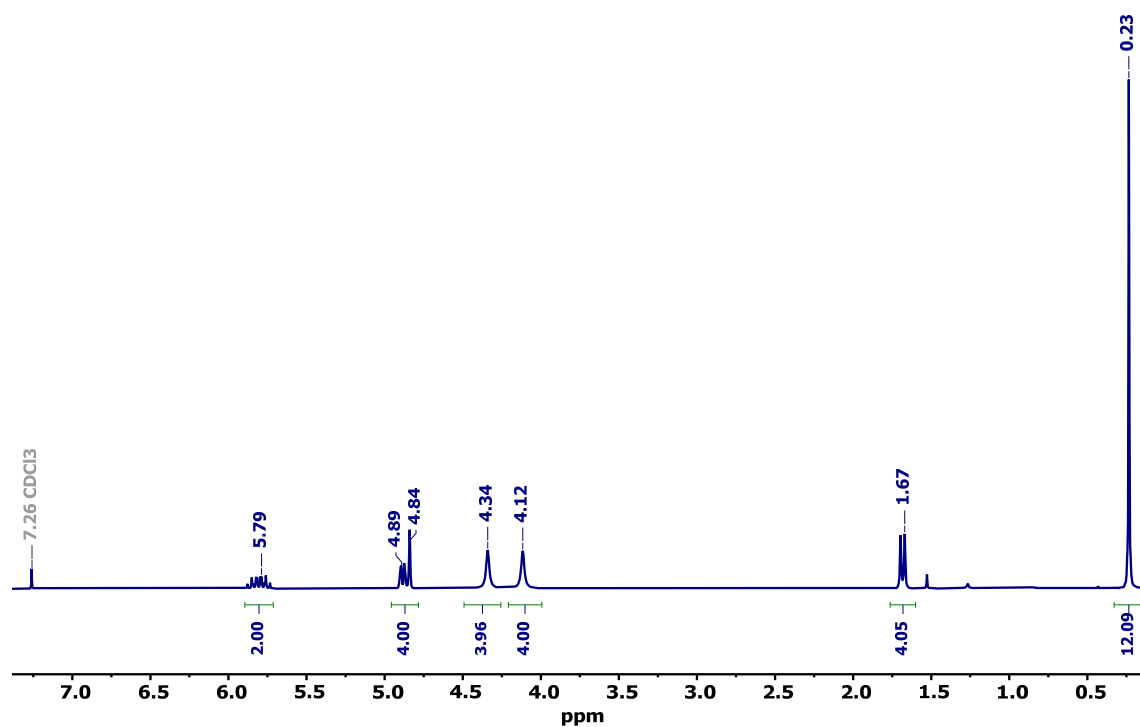


Figure S1: ¹H NMR spectrum of 1,1'-bis(dimethylallylsilyl)ferrocene (**1**, 300 MHz, CDCl₃).

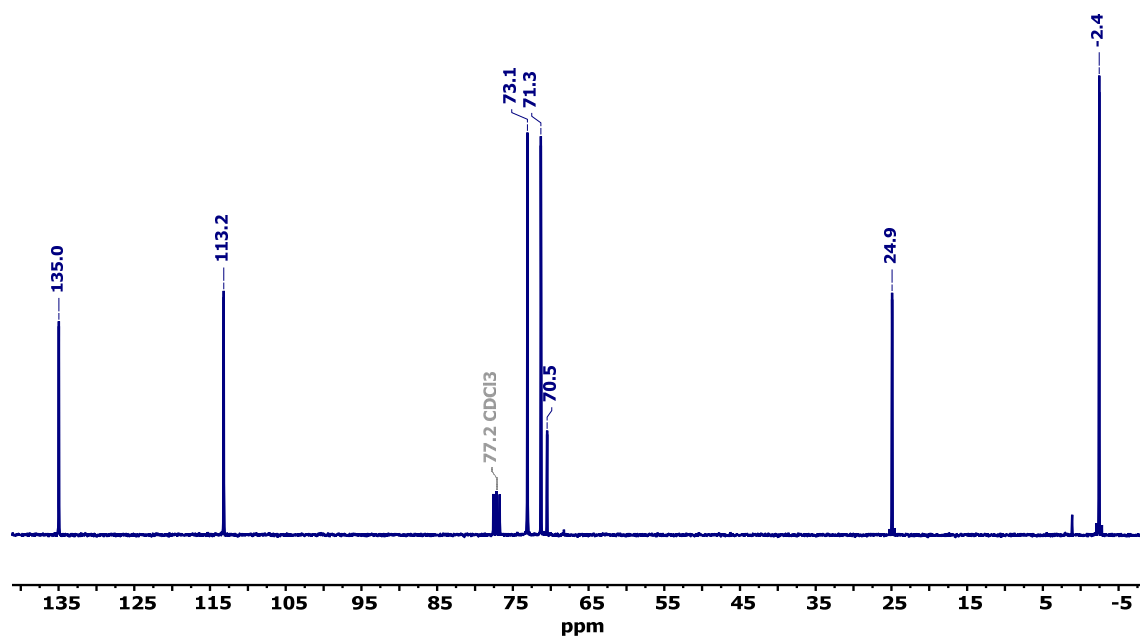


Figure S2: ¹³C{¹H} NMR spectrum of 1,1'-bis(dimethylallylsilyl)ferrocene (**1**, MHz, CDCl₃).

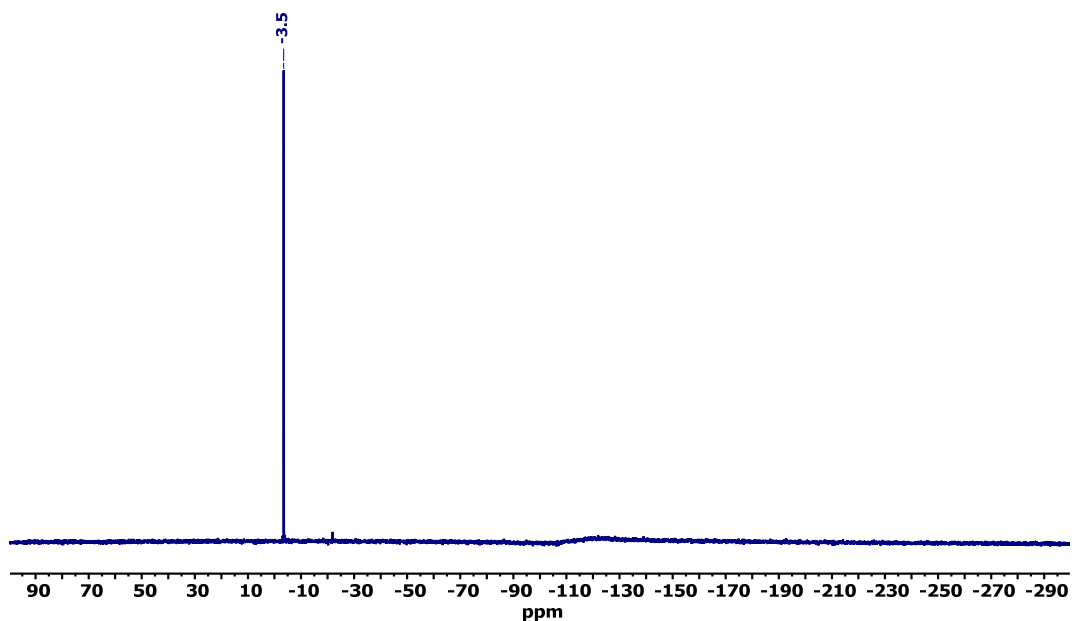


Figure S3: $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of 1,1'-bis(dimethylallylsilyl)ferrocene (**1**, 59.6 MHz, CDCl_3).

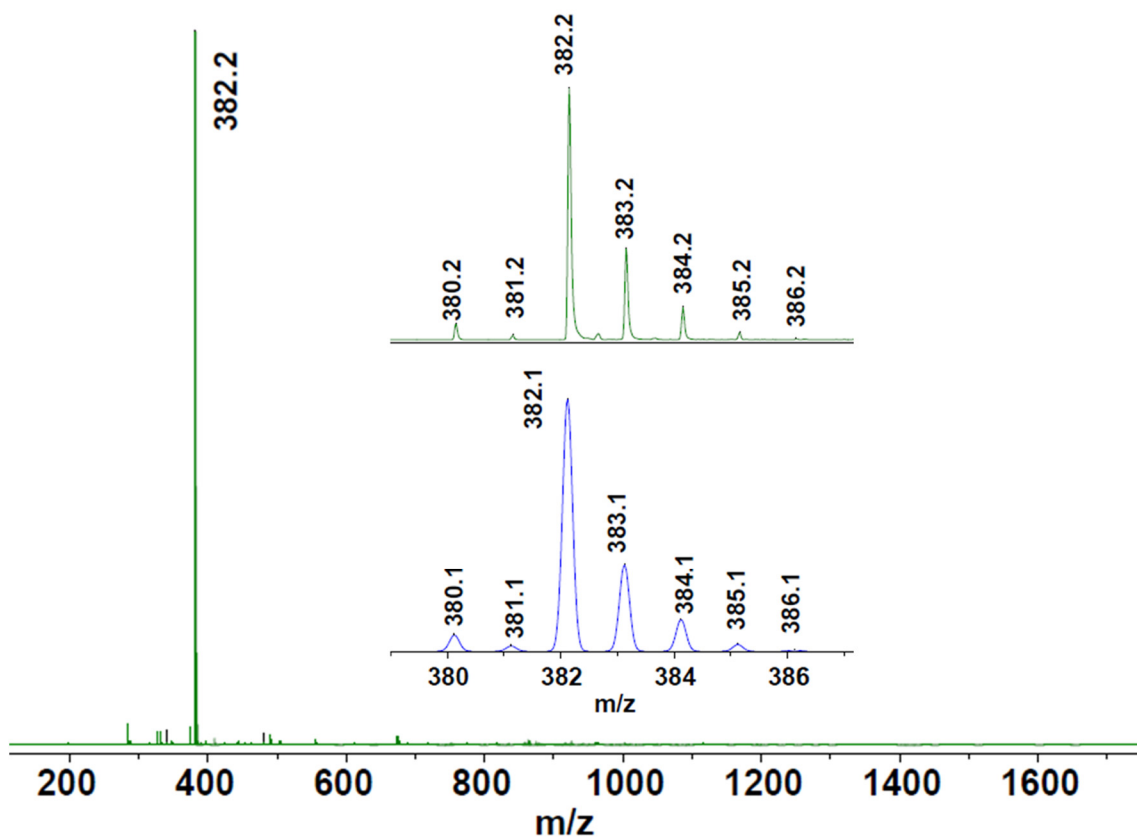
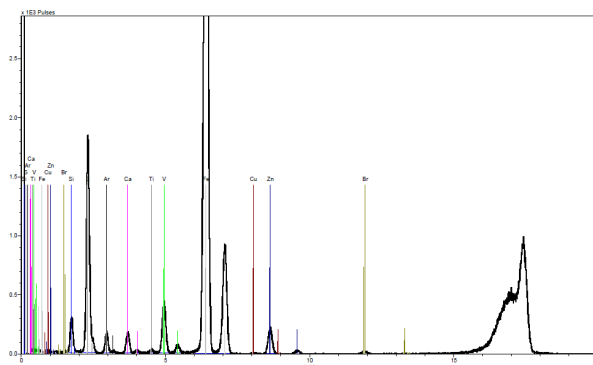


Figure S4: MALDI-TOF mass spectrometry of 1,1'-bis(dimethylallylsilyl)ferrocene (**1**). Inset: isotopic distribution of the molecular ion peak (top: experimental; bottom: calculated).

3. Characterization of polysulfide materials 2 and 3

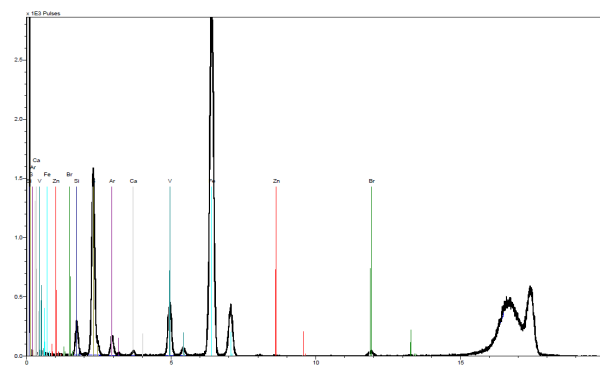
Table S1: Elemental analysis of materials 2 and 3. ^aCalculated values.

Material	S _g :1 wt %	%C	%H	%S	%Fe+Si ^d	Estimated average number of S atoms per Fc[Si(CH ₃) ₂ (-CH ₂ -CH-CH ₂ -)] ₂ unit ^d
2	50:50	36.68	4.69	37.90	20.73	8
3	70:30	25.86	3.37	55.69	15.08	16



Element	Line	Conc. mg/L	Sigma mg/L	RSD %	LLD mg/L	Net area	Backgr.	Chi
Si	K12	193.7	3.4	1.7	2.8	6236	887	1.59
S	K12	358.9	2.9	0.8	1.0	42436	1494	5.89
Ca	K12	8.65	0.17	2.0	0.14	4454	603	0.98
Ti	K12	0.677	0.048	7.1	0.080	666	693	1.08
V (IS)	K12	10.00	0.13	1.3	0.07	12398	918	1.79
Fe	K12	94.40	0.49	0.5	0.04	225290	983	31.45
Cu	K12	0.069	0.006	9.2	0.010	281	173	0.73
Zn	K12	1.537	0.023	1.5	0.009	7311	197	2.61
Br	K12	0.112	0.005	4.4	0.005	846	163	1.03

Figure S5: Quantitative TXRF analyses for material 2.



Element	Line	Conc. mg/L	Sigma mg/L	RSD %	LLD mg/L	Net area	Backgr.	Chi
Si	K12	168.2	3.0	1.8	2.4	5613	735	2.40
S	K12	297.6	2.4	0.8	0.8	36463	1129	6.37
Ca	K12	1.459	0.076	5.2	0.106	779	353	1.14
V (IS)	K12	10.00	0.12	1.2	0.05	12847	478	1.59
Fe	K12	39.22	0.23	0.6	0.02	96985	410	9.44
Zn	K12	0.049	0.005	9.3	0.007	244	123	3.60
Br	K12	0.170	0.006	3.3	0.005	1331	162	0.90

Figure S6: Quantitative TXRF analyses for material 3.

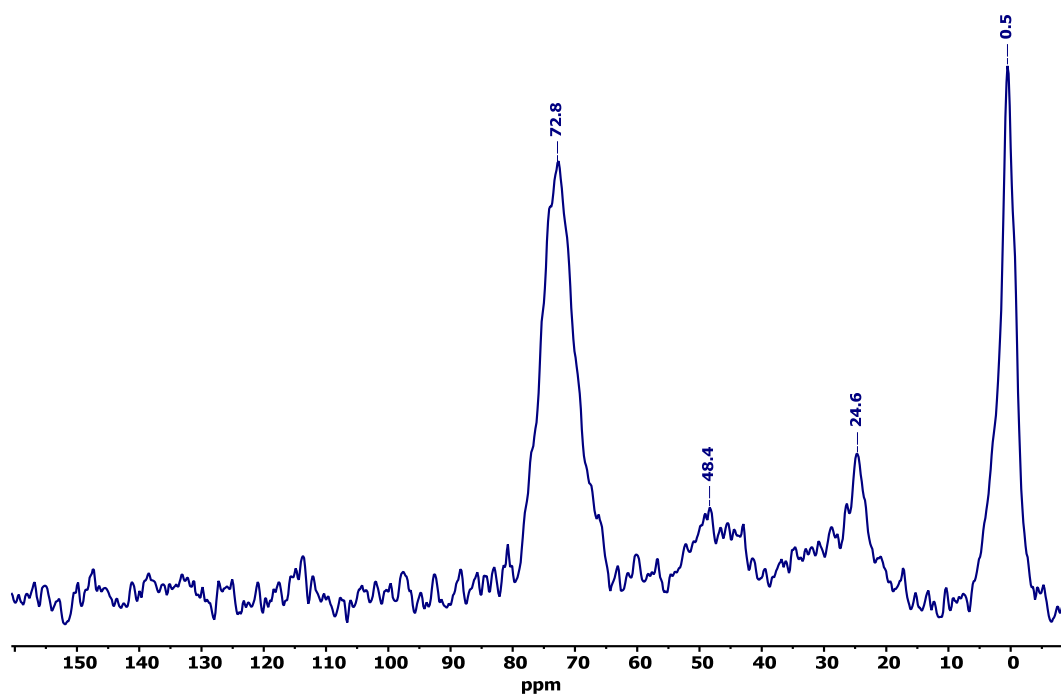


Figure S7: Solid-state ^{13}C CP/MAS NMR spectrum of material 2.

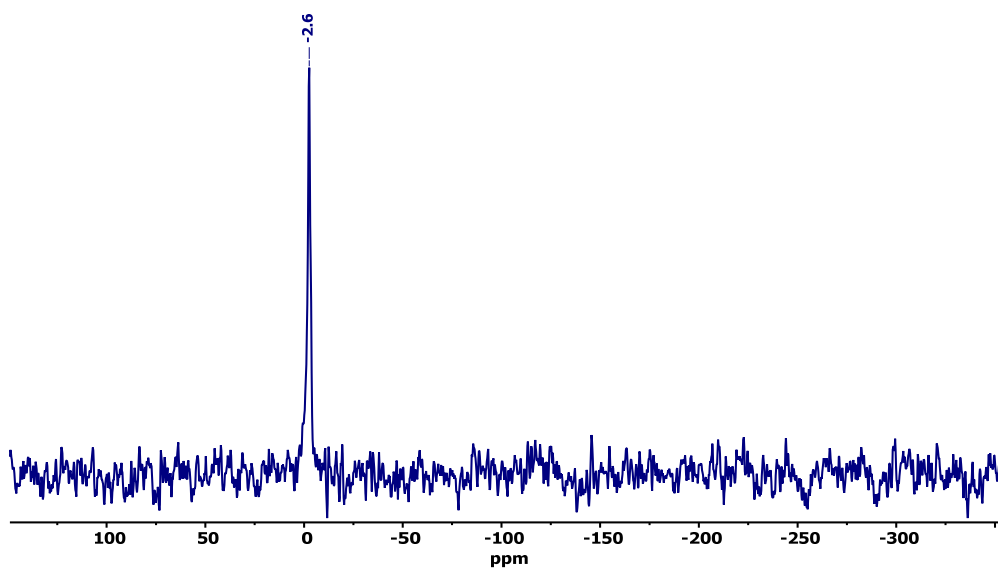


Figure S8: Solid-state ^{29}Si CP/MAS NMR spectrum of material 2.

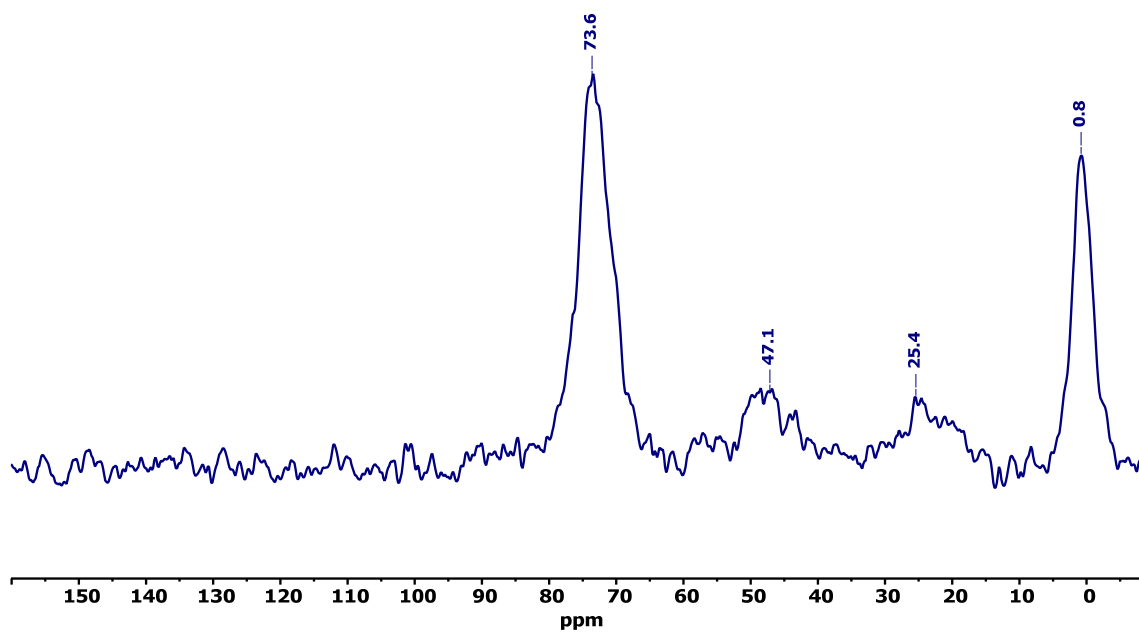


Figure S9: Solid-state ^{13}C CP/MAS NMR spectrum of material **3**.

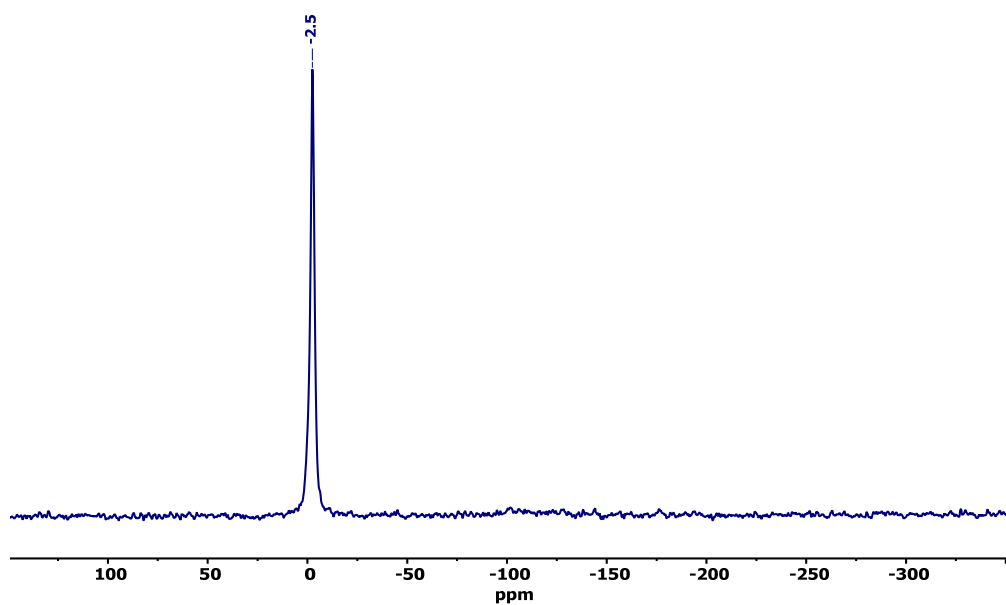


Figure S10: Solid-state ^{29}Si CP/MAS NMR spectrum of material **3**.

X-ray Photoelectron Spectroscopy (XPS):

In the Si 2p spectra, two signals at around 100 and 102 eV have been assigned to Si-C and Si-O environments,³ respectively (Figure S9A). The Si-C bonds were associated with the allylsilane chains while the Si-O signal was attributed to pollution (e.g. silicates) which further agrees with the presence of O atoms (Figure S9B).

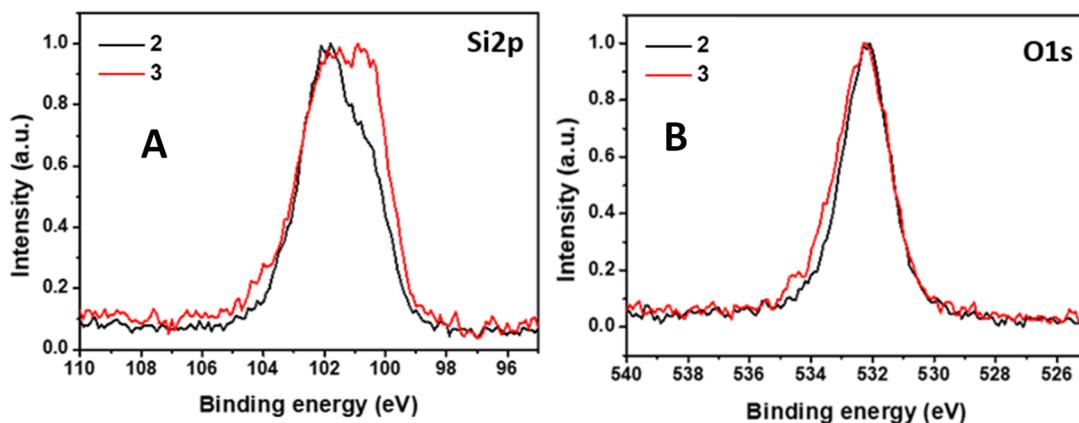
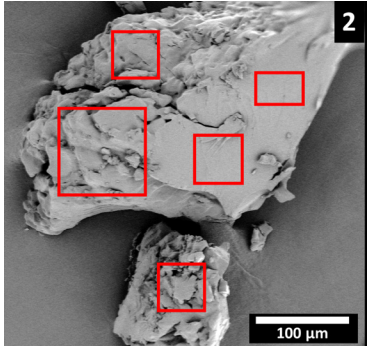
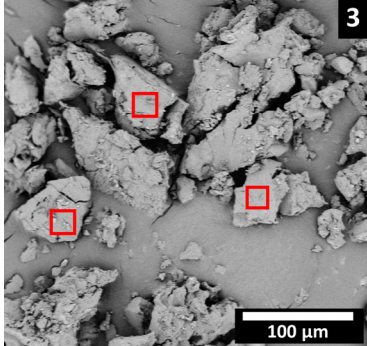


Figure S11: XPS spectra of materials **2** and **3** in the A) Si 2p region and B) O 1s region.

Energy Dispersive X-Ray analysis (EDX):

Table S2: Relative atomic content obtained from various EDX spectra acquired in different regions of materials **2** and **3**, as indicated with red boxes in the SEM images.

Material	S (at. %)	Fe (at. %)	S/Fe ratio	Mean \pm average
	17.57	2.96	5.94	6.9 \pm 0.8 %
	17.48	2.37	7.38	
	19.12	2.38	8.03	
	18.4	2.46	7.48	
	18.99	3.05	6.23	
	16.8	2.4	7	
	39.33	2.44	16.11	15.8 \pm 0.6 %
	46.83	3.1	15.09	
	41.69	2.64	15.8	
	30.14	1.83	16.47	

³ A. Kaur, P. Chahal, T. Hogan, Selective Fabrication of SiC/Si Diodes by Excimer Laser Under Ambient Conditions. *IEEE Electron Device Lett.*, 2016, **37**, 142-145 (DOI: 10.1109/LED.2015.2508479).

Thermogravimetric analysis (TGA):

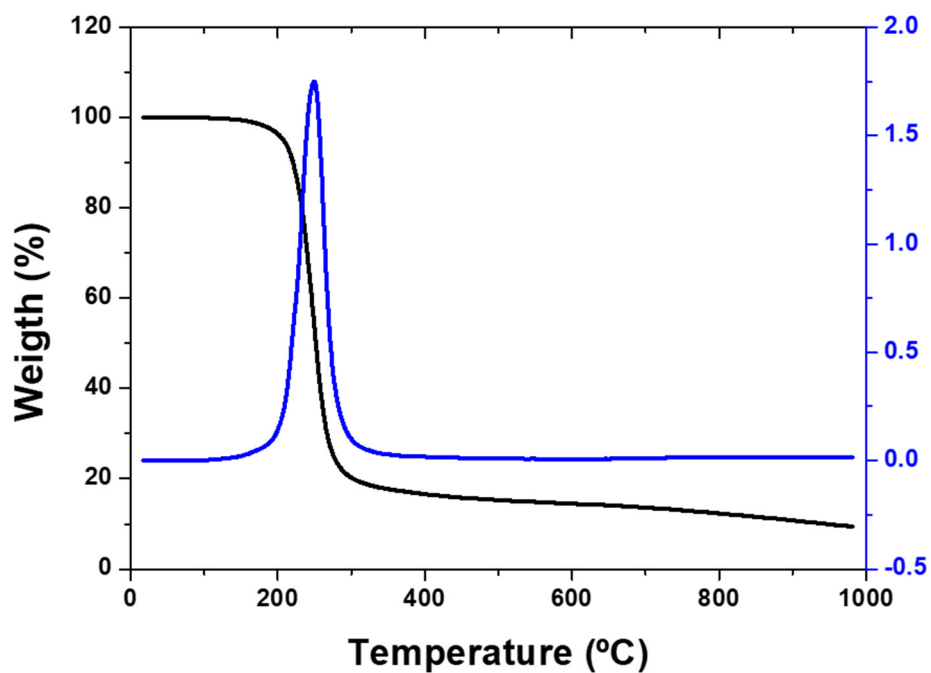


Figure S12: TGA analysis of material 2.

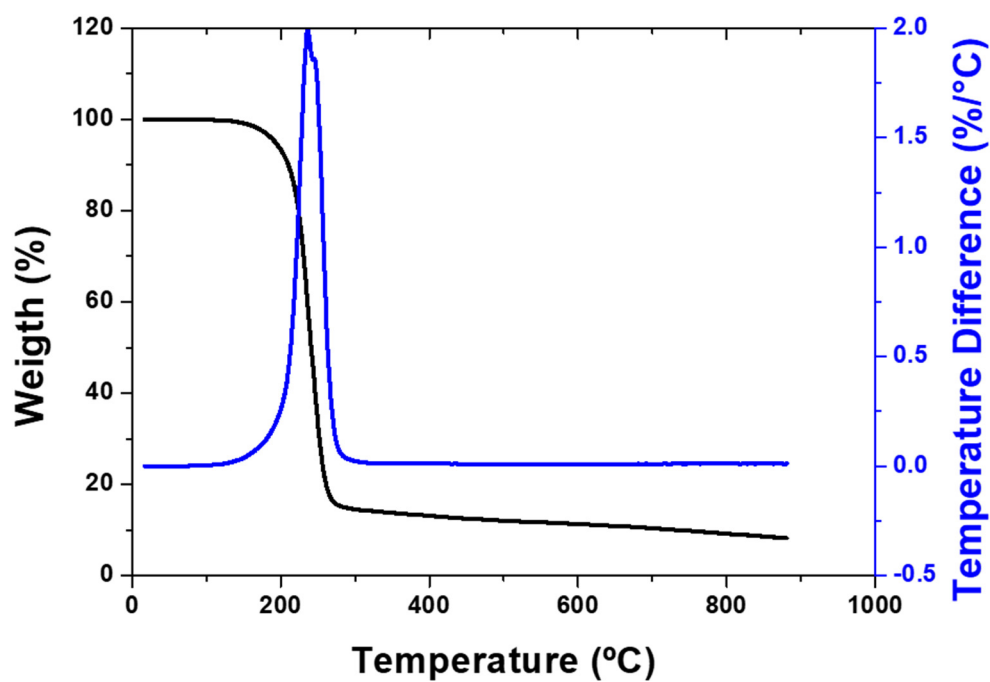


Figure S13: TGA analysis of material 3.

4. Electrochemistry of compound 1 and materials 2 and 3

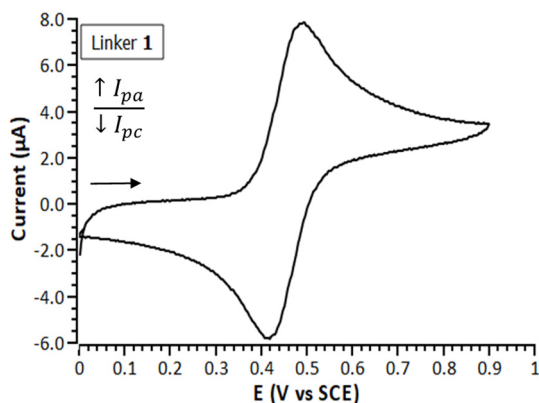


Figure S14: Cyclic voltammogram of compound **1** measured with a gold-disk working electrode, in a 10^{-1} M CH_3CN solution of $[\text{n-Bu}_4\text{N}][\text{PF}_6]$, at 100 mV/s (the first cycle of 20 is shown).

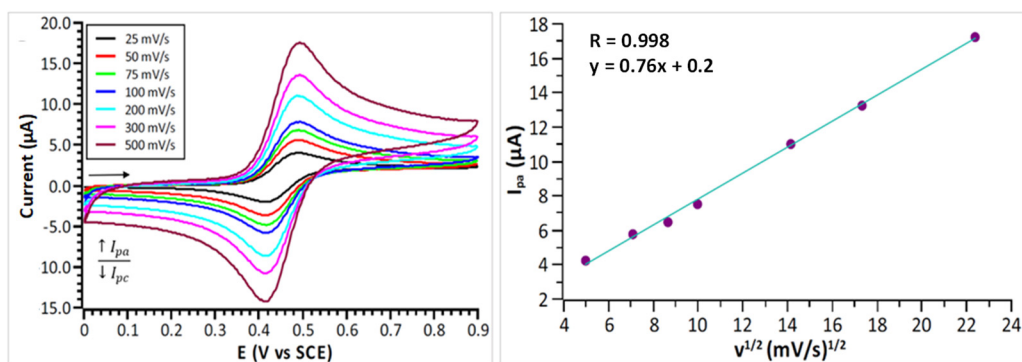


Figure S15: A) CV responses at different scan rates of compound **1** (measured in 0.1M $[\text{n-Bu}_4\text{N}][\text{PF}_6]/\text{CH}_3\text{CN}$, with an Au electrode, vs SCE). B) Plot of peak current versus $v^{1/2}$ (v = scan rate) for compound **1**.

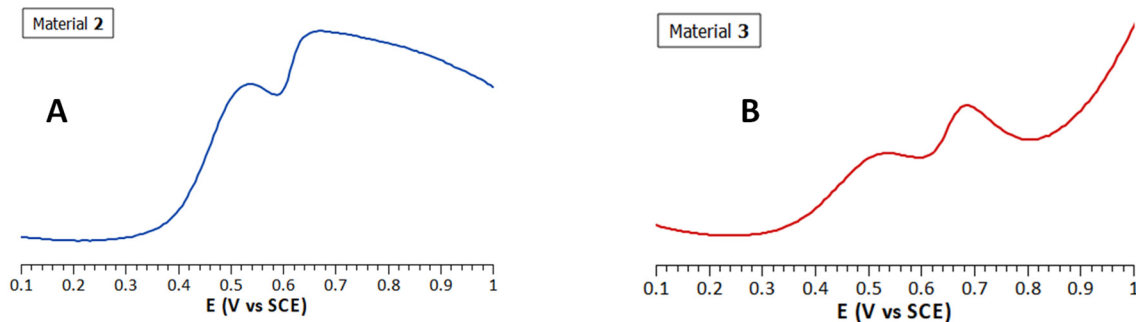


Figure S16: Square wave voltammograms of: materials **2** (A) and **3** (B) measured with a carbon paste working electrode, in a 10^{-1} M CH_3CN solution of $[\text{n-Bu}_4\text{N}][\text{PF}_6]$.

Compound **1** recognition ability was tested by preparing CH₃CN solutions containing 10⁻¹ M [n-Bu₄N][PF₆] and 10⁻³ M of compound **1**. Hg²⁺ and Cd²⁺ recognition studies were performed by consecutive additions of variable amounts of each cation salt in CH₃CN solution (same amounts as the ones used for testing material **2**). No changes in the SWVs of compound **1** were observed for the addition of Hg²⁺ and Cd²⁺, as can be seen in Figure S17, confirming that in material **2** the sulfur atoms are the ones that interact with the soft metals. In addition, the presence of the ferrocenyl units in the new materials obtained allows the electrochemical investigation of these recognition processes, therefore evidencing the synergistic sulfur-ferrocene effect.

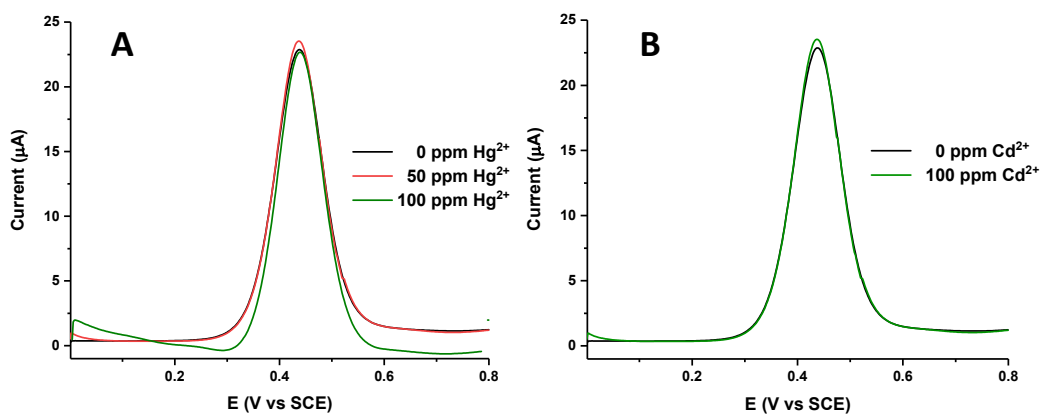


Figure S17: Evolution of the SWV of solutions prepared with compound **1** (10⁻³ M) and [n-Bu₄N][PF₆] (10⁻¹ M), when increasing amounts of Hg²⁺ (A) and Cd²⁺ (B) cations are added.